Mentha viridis oil as a green effective corrosion inhibitor for mild steel in 1 M HCl medium

J. Lazrak,¹ R. Salim,¹ N. Arrousse,¹ E. Ech-chihbi,¹ F. El-Hajjaji,^{1*} M. Taleb,¹ A. Farah² and A. Ramzi²

¹Engineering Laboratory of Organometallic, Molecular Materials and Environment, Faculty of Science, University Sidi Mohamed Ben Abdellah, Po. Box 1796, Fez, Morocco ²Laboratory of Organic and Applied Chemistry, Faculty of Science and Technology, University Sidi Mohamed Ben Abdellah, Fez, Morocco *E-mail: <u>el.hajjajifadoua25@gmail.com</u>

Abstract

The *Mentha spicata* var. *viridis* L. essential oil (MVEO) was analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry GC/MS, which show that it consists mainly of carvone (45.83%), limonene (17.80%) and 1,8-cineole (9.02%). This oil was investigated as corrosion inhibitor for mild steel in 1 M HCl solution by the weight loss measurements, the potentiodynamic polarization (PP) and the electrochemical impedance spectroscopy (EIS) techniques. The results showed that MVEO is a good corrosion inhibitor with inhibition efficiency reached to 85% at concentration of 1 g/L. The polarization curves indicated that MVEO acted as mixed type inhibitor with anodic prevalence. The adsorption of the studied inhibitor on the mild steel surface obey Temkin isotherm and the E_a and ΔG_{ads}^0 values confirmed a physical adsorption processes of this inhibitor. In addition, the structural and electronic properties of the major components of this oil were calculated using the density functional theory (DFT) at B3LYP/6-31G (d, p) level, in order to gain further insight into the adsorption behavior and inhibition mechanism for this plant.

Keywords: Mentha spicata var. viridis L., chromatography, EIS, corrosion inhibition, mild steel, Temkin isotherm, density functional theory.

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1. Introduction

Corrosion is the degradation of metals and their alloys due to a chemical or electrochemical environment. The consequences of this phenomenon are very serious, especially, in industries: cessation of the production, replacement of corroded parts, accidents, and risks of pollution. Indeed, most organic compounds have good anticorrosive action, can be a veritable solution for this problem, particularly, in aqueous mediums. However, the majority of them are highly toxic to humans and environment. These harmful effects lead us to investigate an ecofriendly compound such us essential oils and plant extracts, which are considered as a source of green corrosion inhibitors. In this context, the inhibition effect of *Mentha* essential oil as corrosion inhibitor has been studied by some researchers [1-5]. It is a perennial plant of the *Lamiaceae* family, of the genus *Mentha*, cultivated as an aromatic plant [6]. Its essential oil is rich in carvone, giving it a fresh and mentholated scent. It has a great economic importance, especially in the aroma, perfume and pharmaceutical industries.

The present work focuses on the investigation of *Mentha spicata* var. *viridis* L. essential oil (MVEO) as corrosion inhibitor for the mild steel in molar hydrochloric acid medium using various experimental techniques: weight loss, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS). This study was accompanied by a complementary theoretical approach using DFT/B3LYP 6-31G (d, p) basis set.

2. Materials and methods

2.1. Extraction of the essential oil

The samples of *Mentha spicata* var. *viridis* L. were collected in an experimental plot of the Faculty of Science and Technology – Sidi Mohamed Ben Abdellah University, Fez. The MVEO was achieved by hydro-distillation using Clevenger-type system. As well, the distillation of each samples lasted approximately 2 h. For each distillation, a mixture of 200 g of plants was used. The average oil contents were calculated from the dry matter and expressed in mL/100 g (v/w). Moreover, the oil obtained was analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS).

2.2. Gas chromatography (GC) analyses

GC analyses were performed on a Hewlett-Packard (HP 6890) gas chromatograph (FID), equipped with a HP-5 capillary column ($30 \text{ m} \times 0.25 \text{ mm}$, 0.25 µm). The temperature was programmed from 50°C after 5 min initial hold to 250°C at 4°C/min. The carrier gas was N₂ (1.8 mL/min) and split mode was used (ratio: 1/50, Flow: 72.1 mL/min). Temperature of injector and detector were 275°C. Diluted samples (1/50 in methanol) of 1.2 µL were injected manually.

2.3. Gas chromatography-mass spectrometry (GC/MS) analyses

GC/MS analyses were evaluated on Hewlett-Packard equipped with a HP-5MS (Crosslinked 5% PHME Siloxane) capillary column (30 m × 0.25 mm *i.d.*, 0.25 μ m film thickness) which their temperature controlled from 50 to 250°C at 2°C/min, coupled with a mass spectrometer (HP 5973). The carrier gas was He (1.5 ml/min) and used split mode (ratio: 1/74.7, Flow: 112 ml/min). The components were identified by further confirming their identities MS (Library of NIST98 Spectra). The MS operating parameters were ionization voltages 70 eV, ion source temperature 230°C and scan mass range 35–450 amu.

2.4. Materials

The corrosion tests were carried out on a rectangular surface of 1 cm² area, cut from sheets of mild steel ((wt.%):0.09 P, 0.38 Si, 0.01 Al, 0.05 Mn, 0.21 C, 0.05 S and balance of Fe).

The samples were initially polished with several grades of emery papers (grades 400, 600, 800, 1000, 1200 and 1500), cleaned by distilled water and decreased with ethanol at hot air. The appropriate concentrations tested ranging between 1 and 0.2 g/L, were prepared by dilution of an analytical reagent grade 37% HCl with bi-distilled water.

2.5. Weight loss study

The weight loss study was performed on rectangular steel samples (length = 2 cm, width = 1 cm, thickness = 0.2 cm) in 1 M HCl solution at different concentrations of MVEO and immersed for 6 hours in acid solution.

The corrosion rate (W_{corr}) and the inhibition efficiency (η_{WL} %) were calculated by equations 1 and 2:

$$W_{\rm corr} = \frac{\Delta m}{St} \tag{1}$$

$$\eta_{\rm WL}\% = \frac{W_{\rm corr} - W_{\rm corr/inh}}{W_{\rm corr}} \cdot 100$$
⁽²⁾

where Δm is the weight loss, *t* the immersion time and *S* the surface of the sample. Whereas, W_{corr} and $W_{\text{corr/inh}}$ are respectively the corrosion rate without and with inhibitor.

2.6. Electrochemical study

Electrochemical techniques were carried out in a conventional three-electrode cell connected to a Versa STAT 4 potentiostat and analyzed with VersaStudio software. The electrochemical cell contains the mild steel sample as a working electrode; the platinum electrode as an auxiliary electrode and an Ag/AgCl as a reference electrode. Before each experience, the working electrode was immersed in the tested solution during half hour until the open-circuit potential (E_{ocp}) showed steady-state.

The intensity-potential (IE) curves acquired from potentiodynamic polarization experiments were recorded $\pm 250 \text{ mV}$ from the open-circuit potential at 298 K with a scan rate of 1 mV·s⁻¹. Moreover, the corrosion parameters such as cathodic Tafel slope β_c , corrosion current density i_{corr} , and corrosion potential E_{corr} were obtained by extrapolation from cathodic Tafel linear segment [7] using Ec-Lab Express software. In addition, the electrochemical impedance experiments were realized in the frequency range domain from 100 kHz to 100 mHz, with a small perturbation amplitude of 10 mV peak to peak, at the open circuit potential. Furthermore, the impedance spectra were analyzed according to an appropriate equivalent circuit using ZView 2.80 simulation software and presented in Nyquist and Bode representations.

2.7. Computational details

In order to understand the experimental behaviour of the studied essential oil as a mild steel corrosion inhibitor in hydrochloric acid medium, quantum chemistry calculations were

performed to evaluate the inhibition performance of the three main components of this oil, namely: carvone, limonene and 1,8-cineole. Indeed, the geometries of these three compounds were optimized, using density functional theory (DFT) at B3LYP/6-31G (d, p) [8] basis set by GAUSSIAN 09 software [9]. Accordingly, a number of quantum decriptors, such as: the energies of lowest unoccupied and molecular orbital (E_{HOMO} and E_{LUMO}), the energy gap (ΔE), the dipole moment (μ), the absolute electronegativity (χ), the absolute hardness (η), the softness σ , the ionization potential (*IP*), the electron affinity (*EA*) and the fraction of electrons transferred (ΔN), were calculated in gas and aqueous phases [10].

3. Results and Discussion

3.1. Essential oil composition

The analysis of MVEO by GC–MS technique allowed the identification of thirty-four components, which represented 94.53% in the total of the essential oil composition. The percentages of these components are summarized in Table 1.

Component	%
α-Pinene	1.41
Camphene	0.22
Sabinene	1.4
β-Pinene	2.02
Myrcene	1.01
3-Octanol	1.05
<i>p</i> -Cymene	0.71
Limonene	17.80
1,8-Cineole	9.02
(Z) - β -Ocimene	0.20
cis-Sabinene hydrate	1.60
Linalool	0.40
cis-p-Menth-2-en-1-ol	0.13
cis-Limonene oxide	0.16
trans-Limonene oxide	0.11
Borneol	0.16
δ-Terpineol	0.42

Table 1. Chemical compound of MVEO.

Component	%
4-Terpineol	1.36
α-Terpineol	0.51
Dihydrocarveol	1.73
cis-Dihydrocarvone	1.94
trans-Carveol	0.46
cis-Carveol	0.65
Pulegone	0.36
Carvone	45.83
Isobornyl acetate	0.10
iso-Dihydrocarveol acetate	0.26
β-Bourbonene	0.91
β-Elemene	0.36
β-Caryophyllene	1.25
Germacrene D	0.26
Germacrene A	0.25
Spathulenol	0.12
Caryophyllene oxide	0.36
Total identified	94.53

The MVEO containing three products as major components, which are: the carvone (45.83%), the limonene (17.80%) and the 1,8-cineole (9.02%). The chemical structures of these compounds are presented in Table 2.

Table 2. Major constituents of MVEO.

Name	Molecular formula	Structure	Formula weight (g·mol ⁻¹)
Carvone	$C_{10}H_{14}O$		150.22

Name	Molecular formula	Structure	Formula weight (g·mol ⁻¹)
Limonene	C10H16		136.24
1,8-Cineole	C ₁₀ H ₁₈ O		154.249

3.2. Effect of concentration

3.2.1 Weight loss study

The MVEO inhibition performance were evaluated by weight loss measurement after 6 h of immersion at various concentrations in 298 K. The corrosion rate and inhibition efficiency for mild steel in 1 M HCl offered by MVEO molecule are given in Table 3.

Table 3. Corrosion rate and inhibiting efficacy values of mild steel exhibited for 6 h in 1 M HCl at various concentrations of MVEO, at 298 K.

$C_{\mathrm{inh}}\left(\mathrm{g/L} ight)$	W _{corr} (mg/cm ² ·h)	ղաւ%
HCl 1 M	0.6722	_
1	0.0957	85.76
0.8	0.1464	78.21
0.6	0.1629	75.76
0.4	0.1779	73.54
0.2	0.1952	70.96

Table 3 shows that the inhibition efficiency increases with the MVEO concentration to attain 85.76% at optimum concentration of 1 g/L. This behaviour may be due to the increased surface area covered by the molecules adsorbed on the steel surface, which decreases the corrosive environment and their contact with the steel samples [11].

3.2.2. Potentiodynamic polarisation study

The intensity–potential curves for mild steel in 1 M HCl with and without the MVEO concentrations ranged from 0.2 to 1 g/L at 298 K are shown in Figure 1.



Figure 1. Intensity–potential curves of mild steel in 1 M HCl with various concentrations of MVEO at 298 K.

It can be seen from Figure 1 that the addition of MVEO oil decreases both cathodic and anodic currents, which can be explained by the prevention of the mild steel against the acid attack. This observations suggests that the present essential oil molecules can form a protective film onto the mild steel surface [10, 12, 13].

The cathodic branch, in the absence and presence of MVEO inhibitor are well defined Tafel lines, which means that the hydrogen evolution reaction is activation controlled. Therefore, the decrease of hydrogen ion in the cathodic area of the mild steel surface, essentially means a charge transfer mechanism [14, 15]. The addition of MVEO to the corrosive medium leads to a small modification in the cathodic Tafel slopes (β_c). Indeed, the decrease observed for the cathodic area can be explained by the reduction of the surface area and therefore a reduction for the hydrogen evolution without influencing the reaction mechanism.

Besides, a slight change in the corrosion potential (E_{corr}) towards the anodic branch is registered indicates that our oil inhibits both hydrogen evolution and mild steel dissolution. This displacement was less than 85 mV which lead us to suggest that MVEO act as mixed type inhibitor [16].

Furthermore, in the anodic range for potentials above -0.360 V/Ag/AgCl, a sharp increase in the partial anodic currents were observed. This potential is called desorption potential E_d or a non-polarization potential. The increase in current density after the E_d

potential is often interpreted by the dissolution of iron, resulting in the desorption of the inhibitor film from the electrode surface [16, 17].

The corrosion potential (E_{corr}) values, the corrosion current density (i_{corr}), cathodic Tafel slope (β_c) and the inhibition efficiency (η_{PP} %) were obtained by the extrapolation of linear Tafel segments of cathodic curves and summarized in Table 4. The inhibition efficiency (η_{PP} %) attained from potentiodynamic polarization measurements is calculated by equation 3:

$$\eta_{\rm PP} \% = \left(\frac{i_{\rm corr} - i_{\rm corr/inh}}{i_{\rm corr}}\right) \tag{3}$$

where $i_{\text{corr/inh}}$ and i_{corr} are the corrosion current densities values with and without inhibitor, respectively.

Table 4. Electrochemical parameters obtained from polarization plots of mild steel in 1 M HCl with and without different concentrations of MVEO at 298 K.

	Tafel							
Medium	Cinh (g/L)	Ecorr (mV vs. Ag/AgCl)	i _{corr} (µA∙cm ⁻²)	$egin{array}{c} \beta_c \ (mV \cdot dec^{-1}) \end{array}$	ηрр %			
HCl 1 M	—	-408	816	-150	—			
	1	-383	144	-129	82			
	0.8	-402	179	-121	78			
MVEO	0.6	-403	211	-115	74			
	0.4	-395	296	-106	64			
	0.2	-385	328	-111	60			

It can be observed from Table 4 that the addition of different concentrations of MVEO leads to a considerable decrease in the current density i_{corr} with the increase of MVEO concentrations. Therefore, the inhibition efficiency η_{PP} % increases until reaches 82% at the optimum concentration of 1 g/L, indicating the formation of a more complete and stable adsorbed film onto the surface of the working electrode.

Further, the values of the cathodic Tafel slopes did not change significantly with the addition of MVEO, indicating that the mechanism of discharge of the hydrogen evolution is not affected by the inhibitor [18].

3.2.3. EIS study

In order to confirm the results taking out from the potentiodynamic polarization technique and to get more information on the inhibition mechanisms, the EIS measurements were performed at corrosion potential and allow to evaluate the performance of the inhibitor against mild steel corrosion. The Nyquist and Bode plots for mild steel in 1 M HCl solution alone and in presence of MVEO are presented respectively in Figures 2 and 3.



Figure 2. Nyquist and Bode diagrams of mild steel in 1 M HCl at 298 K.



Figure 3. Nyquist and Bode diagrams of mild steel in 1 M HCl at different concentrations of MVEO.

The EIS spectra plotted for mild steel 1 M HCl presented in Figure 2, shows only one depressed capacitive loop to the higher frequency range (HF) with one capacitive time constant. In this case, the experimental impedance diagram was adapted to the appropriate equivalent model shown in Figure 4a. In this equivalent circuit, R_s is the solution resistance, R_{ct} present the charge transfer resistance and CPE is the constant phase element. The values of the fitted parameters are presented in Table 5.

Table 5. Fitting results of EIS data for mild steel in 1 M HCl in the absence of MVEO.

Medium	$R_{\rm s} \left(\Omega \cdot {\rm cm}^2 \right)$	$R_{\rm ct}$ ($\Omega \cdot {\rm cm}^2$)	CPE (µF·sn ⁻¹ ·cm ⁻²)	$C_{\mathrm{dl}}(\mu\mathrm{F}\cdot\mathrm{cm}^{-2})$	<i>n</i> dl
1 M HCl	1.033	49.94	277.24	105.8	0.815

The constant phase element (CPE) is used to replace the double layer capacitance (C_{dl}) in order to take into account, the heterogeneity of the electrode surface resulting from surface roughness, and thus to give a more precise fit. The impedance is given by equation 4:

$$Z_{\rm CPE} = Q^{-1} (j\omega)^{-n} \tag{4}$$

where *Q* is proportionality coefficient of CPE (μ F·sn⁻¹), *n* is an exponent associated with the phase shift, *j* is the imaginary number and ω is the angular frequency in rad·s⁻¹.

The double layer capacitance (C_{dl}) was determined by equation 5:

$$C_{\rm dl} = (QR_{\rm ct}^{1-n})^{1/n}$$
(5)



Figure 4. Equivalent circuit used to fit the impedance spectra for mild steel in 1 M HCl solution without and with MVEO.



Figure 5. Nyquist and Bode diagrams for the mild steel interface in a 1 M HCl + 1 g/L solution in inhibitor MVEO (...) experimental curve; (-) fitted curve using structural model in Figure 4a.

To simulate the behaviour of the essential oil in 1 M HCl medium, different circuits was analysed. However, the model shown in Figure 4a does not allow a good fit of the measured data. Figure 5 shows an example of an experimental and theoretical impedance diagram in the Nyquist and Bode representation in the presence of inhibitor at the concentration of 1 g/L (representative example) modelled by this circuit. Indeed, the

superposition of the experimental and simulated spectrum both in the representation of Nyquist and Bode is clearly observed to be inadequate. A second time constant should, therefore, be introduced for a better simulation of the experimental data as Figure 4b presented.

Figure 3 shows Nyquist plots and Bode diagrams for mild steel in 1 M HCl in the presence of a various concentrations of MVEO. The loops observed on the Nyquist diagrams in the presence of the studied inhibitor could be explained by the superposition of two-time constants, the high-frequency time constant could be attributed to the adsorption of inhibitor molecules on the steel surface, while the second time constant at low frequency could be correlated to the process of charge transfer. In addition, the diameter of the capacitive loop rises with MVEO concentration means that the inhibition performance increases as well. Figure 4b represents the structural model used to describe the electrochemical impedance spectra in the presence of MVEO. As it shown in Figure 6, the experimental data were very well fitted according to this equivalent circuit. This model is valid for all MVEO concentrations and the fitted parameters are also shown in Table 6.



Figure 6. Nyquist and Bode diagrams for the mild steel interface in a 1 M HCl+1 g/L solution in inhibitor MVEO (...) experimental curve; (-) fitted curve using structural model in Figure 4b.

The inhibitory efficacy value (η_{EIS}) for the EIS measurement is calculated from the polarization resistance, using the following equation 6.

$$\eta_{\rm EIS}\% = \left(\frac{R_{\rm p/inh} - R_{\rm p}}{R_{\rm p/inh}}\right) \times 100 = \theta_{\rm EIS} \times 100 \tag{6}$$

where R_p and $R_{p/inh}$ are the polarization resistance values without and with different concentrations of MVEO and θ_{EIS} is the surface coverage rate.

G	D		CPE1		D	C	
Cinh (g/L)	$K_{\rm s}$ ($\Omega \cdot {\rm cm}^2$)	(s ⁿ	$Q_{\rm f}$ $\cdot \Omega^{-1} \cdot {\rm cm}^{-2})$	nf	$K_{\rm f}$ ($\Omega \cdot {\rm cm}^2$)	Cr (μF·cm ^{−2})	
1	1.12		100.67	0.849	64.39	41.08	
0.8	0.79		170.84	0.779	50.42	44.50	
0.6	1.27		240.56	0.744	38.51	48.43	
0.4	0.80		290.96	0.727	35.24	52.19	
0.2	0.87		250.23	0.795	22.58	65.87	
C	CPE2		D.	C.	P		
(g/L)	$Q_{ m dl}$ (s ⁿ · Ω^{-1} ·cm ⁻²)	Ndl	$(\Omega \cdot cm^2)$	$(\mu F \cdot cm^{-2})$	$(\Omega \cdot cm^2)$	η eis (%)	
1	80.35	0.8103	193.2	30.30	257.59	80	
0.8	102.43	0.7739	165.8	31.15	216.42	77	
0.6	170.25	0.7180	158.3	41.20	196.18	74	
0.4	200.12	0.7625	106.0	60.30	141.29	64	
0.2	269.53	0.7931	100.7	105.24	123.28	60	

Table 6. Electrochemical impedance parameters of mild steel in 1 M HCl in the presence of MVEO at various concentrations at 298 K.

Analysis of the calculated electrochemical parameters shows an increase in charge transfer resistance R_{ct} and inhibitor film resistance R_f with increasing concentration. At the same time, we observe a decrease in the pseudo-capacities related to the electrochemical double layer and the adsorption of inhibitor molecules on the surface of the metal in conjunction with the rise of inhibitory efficacy η_{EIS} . This decrease of C_{dl} can be attributed to the formation of a protective layer on the mild steel surface [19]. In addition, the evolution of coefficients of heterogeneity shows almost the same pattern in the presence of the inhibitor studied. Indeed, the increase observed in the values of n_f and n_{dl} with the inhibitor concentrations can be explained with a decrease in surface heterogeneity resulting from the adsorption of inhibitors to the active sites [20].

It should be noted that the inhibitory efficiencies calculated by the EIS method are comparable and goes parallel with those obtained by weight loss measurements and potentiodynamic polarization method, indicating reasonable agreement between the two studied method.

3.2.4 Adsorption isotherms

The determination of an isotherm describes the type of adsorption of a corrosion inhibitor. Therefore, it is very important to provide a significant index of the nature of the metal-inhibitor interaction. The calculations in this section are based on the assumption of a blocking mechanism of action of the corrosion inhibitor. However, we have tested many adsorption isotherms such as Langmuir, El-Awady, Freundlich and Temkin. The values of the surface coverage rate θ_{EIS} are obtained by electrochemical impedance spectroscopy according to Equation 6. Indeed, all these isotherms can be defined by their linearized forms, as illustrated in Table 7 [21–26].

Isotherms	Linear equations
Langmuir	$rac{C_{ ext{inh}}}{ heta} = rac{1}{K_{ ext{ads}}} + C_{ ext{inh}}$
El-Awady	$\log\left(\frac{\theta}{1-\theta}\right) = y \log\left(K_{ads}\right) + y \log\left(C_{inh}\right)$
Temkin	$\theta = \frac{-1}{2a} \ln(K_{ads}) + \frac{-1}{2a} \ln(C_{inh})$
Freundlich	$\ln \theta = \ln \left(K_{ads} \right) + a \ln \left(C_{inh} \right)$

Table 7. The linearized forms of the most common adsorption isotherms.

The standard free energy of adsorption, ΔG_{ads}^0 was calculated according to equation 9:

$$\Delta G_{\rm ads}^0 = -RT \ln \left(1000 \cdot K_{\rm ads} \right) \tag{9}$$

where *R* is the universal gas constant, *T* is the temperature equal to 298 K, K_{ads} is the equilibrium constant of the adsorption process and 1000 g/L present the concentration of water in solution.

Figure 7 illustrate the different adsorption isotherm models using EIS technique and the adsorption parameters deduced from different isotherms and the corresponding values are recorded in Table 8.

It can be seen from Table 8 that the regression coefficient R^2 is perfectly adequate for all four isotherms. Nevertheless, the slope of the Langmuir isotherm is greater than unity (1.12) but stay the closest and reasonable isotherm to explain the adsorption process. This deviation directs us to look for another isotherm that well describes the corrosion process.

From El-Awady isotherm, the parameter deduced 1/y is of the order of 1, which implies that each active compound of the essential oil is replaced by one molecule of water fixed to an active site on the surface of the mild steel during the inhibition process.



Figure 7. Plots of the adsorption isotherm models of MVEO for mild steel surface in 1 M HCl at 298 K obtained from EIS data.

According to Table 8, it should be noted that the K_{ads} value obtained from the three isotherms is very low, except for the Temkin isotherm. Therefore, these three models are rejected, despite the high values of the coefficient of regression R^2 . Consequently, it can be concluded that the adsorption process obeys the Temkin isotherm due to the high value of K_{ads} and the R^2 coefficient. Also, the negative sign of the intermolecular interaction parameter between the essential oil molecules adsorbed on the mild steel surface, which suggests the existence of molecular interactions in the adsorbed layer.

Generally, when ΔG_{ads}^0 values around $-20 \text{ kJ} \cdot \text{mol}^{-1}$, or less negative, the interactions between the charged mild steel surface and the charged essential oil compounds are electrostatic and the adsorption is physical. Whereas, when the values of ΔG_{ads}^0 are close to $-40 \text{ kJ} \cdot \text{mol}^{-1}$ or more negative, in this case, there is a transfer of electrons from the inhibitor molecules to the surface of the metal and the adsorption is chemical [27, 28]. According to the obtained results, the adsorption type of the MVEO essential oil can be adsorbed with physisorption nature.

Isotherms	R ²	Para	meters	$K_{ m ads}, { m L}{\cdot}{ m g}^{-1}$	$\Delta G_{\rm ads}^{\rm 0}$, kJ·mol ⁻¹
Langmuir	0.995	slope	1.12	7.28	-22
El-Awady	0.937	1/y	1.57	8.19	-22
Freundlich	0.949	n	0.19	0.80	-17
Temkin	0.944	а	-3.80	$4.25 \cdot 10^3$	-25

Table 8. Adsorption parameters deduced from various adsorption isotherms of MVEO at 298 K.

3.3. Immersion time effect

The evolution of the inhibiting effect as a function of the immersion time makes it possible to have interesting information on the stability of the inhibitor film. Therefore, we evaluated the influence of this factor basing on electrochemical impedance spectroscopy results. The impedance measurements were carried out during immersion times from 0.5 h to 10 h at 298 K.

The Nyquist diagrams *versus* immersion time in 1 M HCl solution in the absence and presence of 1 g/L of MVEO at 298 K are shown in Figure 8.



Figure 8. Impedance spectra obtained after different immersion time in 1 M HCl solution without (a) and with (b) 1 g/L of MVEO.

According to Figure 8, it can be observed that an increase in the size of the capacitive loop up to four hours of immersion, then, beyond 4 h, a slight decrease in the impedance spectrum diameter was recorded. This behaviour could be explained by the stability of the protective layer formed by the essential oil compounds adsorbed on the metal surface [29, 30]. Moreover, it should be noted that a good correlation between the experimental and

simulated data was obtained by the circuit adopted before (Figure 4b), which perfectly attests to the existence of two relaxation phenomena in the frequency domain exploited. The equivalent circuit parameters are presented in Table 9.

It is clear from Table 7 that after 4 h of immersion, the values of R_{ct} and R_{f} decrease while the values of C_{dl} and C_{f} increase with immersion time.

This behavior can be attributed to an increase in the film's performance up to 4 hours. As a result, it can be suggesting that a protective layer was formed on the steel surface during 4 hours [31].

Medium	Time (h)	$R_{\rm s}$ ($\Omega \cdot {\rm cm}^2$)	$R_{\rm f}$ ($\Omega \cdot {\rm cm}^2$)	$C_{\rm f}$ ($\mu {\rm F} \cdot {\rm cm}^{-2}$)	$\frac{R_{\rm ct}}{(\Omega \cdot \rm cm^2)}$	$C_{\rm dl}$ ($\mu {\rm F} \cdot {\rm cm}^{-2}$)	$R_{ m p}$ ($\Omega \cdot m cm^2$)	ηeis %
	0.5	1.033	_	_	49.94	105.8	49.94	_
	1	0.358	_	_	42.96	331.3	42.96	_
	2	1.097	_	_	41.93	333.7	41.93	_
1 M HCl	4	0.356	_	_	40.94	347.2	40.94	_
	6	0.359	_	_	36.97	409.1	36.97	_
	8	0.363	_	_	32.16	562.6	32.16	_
	10	0.367	_	_	31.90	663.0	31.90	_
	0.5	1.294	02.64	41.08	246.4	30.30	257.59	80.61
	1.0	1.125	69.08	21.27	196.3	25.59	265.38	83.81
	2.0	1.118	101.6	24.28	162.9	27.17	264.50	84.14
MVEO	4.0	1.120	112.4	18.69	159.9	22.42	272.30	84.96
	6.0	1.103	115.9	34.50	146.0	28.87	261.90	85.88
	8.0	1.098	126.9	47.25	128.4	47.15	255.30	87.40
	10.0	1.083	118.8	57.79	124.2	54.83	243.00	86.87

Table 9. Impedance data for mild steel in the absence and presence of 1 g/L of MVEO at different immersion periods.

3.4. Temperature effect

Generally, the temperature can be influenced the inhibition efficiency of MVEO for mild steel in a 1 M HCl solution. This inhibition was performed with and without MVEO optimum concentration 1 g/L at a temperature ranging from 303 to 333 K using weight loss experiments. Table 10 shows the variation of the corrosion rate (W_{corr}) and inhibition efficiency (η_{WL} %) of the mild steel at different temperatures.

It can be observed clearly from Table 8 that W_{corr} increases with temperature and the inhibition efficiency η_{WL} % decrease slowly with increasing temperature. Consequently, this could lead to desorption of MVEO from the mild steel surface [21].

Townstreet	Corrosion rate W	····· 0/	
Temperature	blank	MVEO	ηwL %ο
303	0.8638	0.1415	83.62
313	1.1526	0.2538	77.98
323	1.4678	0.5369	63.42
333	2.3332	0.8881	61.93

Table 10. Influence of temperature on the mild steel corrosion at different concentrations in the absence and presence of MVEO at 2 h.

To obtain information on the adsorption process, the activation parameters can be determined from the Arrhenius equation 7 and transition state equation 8:

$$i_{\rm corr} = A e^{\left(\frac{-E_a}{RT}\right)}$$
(7)

$$i_{\rm corr} = \frac{RT}{Nh} e^{\left(\frac{\Delta S^*}{R}\right)} e^{\left(\frac{-\Delta H^*}{RT}\right)}$$
(8)

Where *A* being the Arrhenius pre-exponential constant, E_a is the apparent activation energy, *R* is the gas constant, *T* is the absolute temperature, *h* is the Plank's constant, *N* is Avogadro's number, ΔH^* is the enthalpy of activation and ΔS^* is the entropy of activation.

The Arrhenius plots for the corrosion rate of mild steel are given in Figures 9 and 10. The values of E_a , ΔH^* , ΔS^* , and $E_a - \Delta H^*$ of MVEO are shown in Table 11.



Figure 9. Arrhenius plots $\ln W_{corr}$ vs. 1000/T in 1 M HCl with and without 1 g/L of MVEO.



Figure 10. Arrhenius plots $\ln W_{\text{corr}}/\text{T} vs. 1000/\text{T}$ in 1 M HCl with and without 1 g/L of MVEO.

Table 11. The values of E_a , ΔH^* , ΔS^* and $E_a - \Delta H^*$ of MVEO for mild steel in 1 M HCl in presence and absence of 1 g/L of MVEO.

	Ea (kJ·mol⁻¹)	∆H* (kJ·mol ⁻¹)	$\Delta S^* \\ (\mathbf{J} \cdot \mathbf{mol}^{-1} \cdot \mathbf{K}^{-1})$	$E_{a}-\Delta H^{*}$ (kJ·mol ⁻¹)
Blank	26.95	24.31	-178.42	2.64
1 g/L of MVEO	52.55	49.92	-108.82	2.64

We notice from Table 9 that the activation energy E_a of the inhibited solution increases in the presence of MVEO compared to blank solution; this is explained by the specific interaction between the essential oil and the surface of the mild steel. Moreover, the higher value of the activation energy in the presence of MVEO compared to 1 M HCl solution is often interpreted in the literature by the physisorption of the inhibitor on the mild surface [32, 33]. The positive values of ΔH^* describe that the dissolution reaction is an endothermic process. Also, it can be observed that the high negative value of ΔS^* in the presence of MVEO reflects a decrease of the disorder during the formation of the complex metal/adsorbed compound [34].

The relationship between E_a and ΔH^* values resulted in a constant value equal to 2.64 kJ·mol⁻¹.

$$E_{a} - \Delta H^{*} = RT \tag{9}$$

3.5. Quantum calculations

In favour to get more detail about the interaction of MVEO with the metallic surface, the DFT calculations for the carvone, the limonene and the 1,8-cineoleas major components of this essential oil were carried out, at B3LYP/6-31G(d,p), in gas and aqueous phases.

According to the quantum computation results, the absence of imaginary frequency in the vibrational spectra prove that the equilibrium structures correspond to the minima of total energy $E_{\rm T}$ of the investigated components, which implies that the obtained calculated structures correspond to the optimized final geometries of these molecules, as represented in Figure 11.



Carvone

Limonene

1,8-cineole

Figure 11. The optimised geometries for major components of MVEO, at B3LYP/6-31G (d,p), in gas phase.

Furthermore, the pertinent quantum chemical parameters of the three major components derived from the ground state for the optimized geometries of the investigated essential oil were calculated and summarized in Table 12.

Table 7.	Quantum	chemical	descriptors	of carv	one, limo	nene and	d 1,8-cineole	structures	using	DFT	at
B3LYP/6	-31G (d, p) level of	theory, in ga	as (G) ar	d aqueou	s (A) pha	ases.				

Inhibitor	Phase	<i>Е</i> т (a.u.)	<i>Е</i> номо (eV)	Elumo (eV)	Δ <i>E</i> (eV)	μ (D)	χ (eV)	η (eV)	σ (eV ⁻¹)	ΔN
Carvone	G	-464.715	-6.414	-1.247	5.167	2.927	3.830	2.583	0.387	0.614
	А	-464.723	-6.524	-1.328	5.196	4.234	3.926	2.598	0.385	0.592
Limonene	G	-390.699	-6.134	-0.742	5.392	0.560	3.438	2.696	0.371	0.661
	А	-390.702	-6.117	-0.733	5.384	0.705	3.425	2.692	0.371	0.664
1,8- Cineole	G	-467.161	-6.240	-1.855	4.385	1.290	4.047	2.192	0.456	0.674
	А	-467.164	-6.275	-1.670	4.605	1.900	3.972	2.302	0.434	0.658

In order to give additional indications on the possibility of electron transfer between our molecules and the metal surface, and to determine the electron-rich sites in the studied major components of MVEO, quantum molecular modelling was carried out, which allowed to extract the most relevant molecular reactivity parameters for these three molecules.

A good corrosion inhibitor is one which has a high tendency to donate and receive electrons, in order to bind strongly to the metal surface. By this means, the analysis of the Table 12 indicates that the presence of an oxygen atom in carvone and 1,8-cineole, provokes a higher value of E_{HOMO} and a lower value of E_{LUMO} for these compounds compared to limonene, either in gas or aqueous phases. Indeed, the frontier molecular orbitals HOMO and LUMO provide an idea about the sites of the molecule with the tendency to donate or accept electrons [35]. According to this theory, these two molecules can exchange electrons with the metal surface by increasing their coverage rates on it, resulting in enhanced their corrosion inhibition efficiency compared to 1,8-cineole. As result is supported by the energies gap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) values. The results as indicated in Table 12 follow the order: ΔE (1,8-cineole) < ΔE (carvone) < ΔE (limonene). Chemically, when ΔE decreases, the molecular reactivity increases; which means that 1,8-cineole and carvone in a second degree, could have better interaction performance with the surface of mild steel, as corrosion inhibitors, more than the limonene molecule.

Concerning the dipole moment (μ) and electronegativity (χ), it is well known that a high value of these parameters probably increases the adsorption of the chemical compound on the metal surface [36, 37], which increases the contact surface between the molecule and the metal, thus enhancing the capacity of the corrosion inhibition of the said inhibitor. According to the values collected in Table 12 the high values of these two indices for 1,8-cineole and carvone compared to limonene, could be attributed to the existence of the oxygen atom in these two compounds, which increases their polarity and facilitates the electrostatic interaction happens between the electric field resulting from the charged metal surface and the electric moments of the two inhibitor molecules and probably, contributes to a better adsorption by affecting the process of the charge transfer through the adsorbed layer [38, 39].

Similarly, it can be also observed that the absolute hardness (η) and the softness (σ) evolve in the same trend as the other parameters, which is consistent with the meaning of these two parameters. This implies that 1,8-cineole and carvone are less hard and softer than limonene, which translates into their low values from ΔE which can give them a better reactivity and increase their ability to inhibit the degradation of the metal under study [40].

The electronic density distributions of the HOMO and LUMO orbitals are shown in Figure 12.

As shown in Figure 12, it can be seen from the distribution of the HOMO and LUMO orbitals of the three studied compounds, that the electronic cloud is mainly localized on the benzene rings and on the oxygen atom. Therefore, these molecular sites can be preferentially adsorbed on the surface of the steel. The analysis of the graphs shows also that the red zones assigned to the oxygen atoms correspond to the nucleophilic property, whereas, the blue zones correspond to the electrophilic property. These atoms are very clear on the orbitals of

1.8-cineole and the carvone; indicating that these two molecules can easily form a coordination bonds with iron atoms compared to limonene, which may enhance the adsorption stability and led to an improvement in the inhibition potential of the comparative molecules.

Furthermore, these results can be reinforced by the charge density distribution and localization on the atoms, which provide information on the reactivity sites, as illustrated in Figure 13.



Figure 12. The HOMO and LUMO for carvone, limonene and 1,8-cineole as major components of MVEO, at B3LYP/6-31G (d, p), in gas phase.

According to Figure 13, the mapped data demonstrate that carvone and 1,8-cineole could result in the strong anticorrosion process possibly due to the relatively high surface charge, as compared to limonene. Moreover, the partial atomic charges values in Figure 13 (d, e and f) and their corresponding charge densities displayed by the red areas, in Figure 13 (a, b and c) indicate that the O atoms are more negative charges with (-0.37 C for 1,8-cineole and -0.35 C for carvone), suggesting that these sites are the atoms on which the electrophilic attack would preferably occur [41, 42]. However, the other partial charges carried by the carbon atoms are generally weakly positive or negative which implies that the sites corresponding to these charges, can probably undergo nucleophilic and electrophilic attacks, thus favoring the percentage of interactions of these three molecules with the steel substrate, and therefore, increasing their corrosion inhibiting capacities.



Figure 13. Charge density distribution and localization on the atoms of the carvone (a and d), the limonene (b and e) and the 1,8-cineole (c and f).

Conclusion

In this research, the *Mentha spicata* var. *viridis* L. essential oil (MVEO) was evaluated as a green effective corrosion inhibitor for mild steel in in 1 M hydrochloric acid medium by weight loss measurement, intensity-potential measurements, EIS and DFT calculations. The obtained results lead us to conclude:

- The gravimetric and electrochemical analysis show that *Mentha spicata* var. *viridis* L. essential oil (MVEO) is an effective corrosion inhibitor for mild steel in 1 M HCl.
- The inhibition efficiency of MVEO increases with the rise of concentration and reaches 80% at concentration of 1 g/L.
- The potentiodynamic polarization curves indicate that MVEO acts as mixed type inhibitor with predominantly anodic.

- The impedance spectra obtained in the presence of MVEO inhibitor are characterized by two-time constants which attributed to the formation of inhibitory film (high frequencies) and charge transfer (low frequencies).
- The adsorption of MVEO obeys the Temkin adsorption isotherm.
- The thermodynamic parameters analysis reveals that the adsorption of MVEO onto the mild steel surface follows physical adsorption.
- The DFT calculations provide an explanation of the relationship between molecular structure and anticorrosion efficiency, using the structural and electronic properties of carvone, limonene and 1,8-cineole as the major components of the tested *Mentha* essential oil.

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